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Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.439588](https://doi.org/10.1063/1.439588)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1980

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Citation for published version (APA):
Sawatzky, G. A., & Lenselink, A. (1980). Localized vs delocalized description of photoelectron spectra. *Journal of Chemical Physics*, 72(6), 3748-3753. <https://doi.org/10.1063/1.439588>

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Citation: [The Journal of Chemical Physics](#) **72**, 3748 (1980); doi: 10.1063/1.439588

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Localized vs delocalized description of photoelectron spectra

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(Received 25 July 1979; accepted 4 December 1979)

A model calculation is presented to investigate the conditions under which an excitation of a molecule or solid should be treated in a symmetry restricted or localized manner. The three important quantities in the model, the hole delocalization energy, the response time of the polarizable medium, and the interaction between the hole and the polarizable medium are included as variables. The exact solution is compared to approximations, and ranges of the three above-mentioned quantities are found for which the symmetry restricted or localized solutions yield the best results. It is found that the localized solutions with symmetrization afterwards yield the best results for a surprisingly large range of the three interactions and seems to be the better solution even for describing valence orbital photoelectron spectra.

In a calculation of ionization potentials or excitation energies of molecules or solids as related to photoelectron or optical spectra, it is extremely important to start with Slater determinants of the N , $N-1$, or N^* (excited state) electron system in which the one-electron orbitals are chosen in such a way as to minimize the amount of configuration interaction (CI) required to obtain the correct result. In core electron photoionization or in optical spectra involving lone pair excitations, for example, one can start with either a molecular orbital or a localized description of the hole-state wave function to obtain the excitation energies. In the localized case, one assumes the core hole to be localized on a particular site allowing the outer valence electrons to move in and screen the core hole. After having determined this many-electron wave function, one can allow the core hole plus its polarization cloud to delocalize according to the symmetry of the molecule or solid. This is the procedure used in polaron or, more specifically, electronic polaron theory in solids. It results in reduced band gaps and bandwidths relative to a one particle picture because of the "Franck-Condon" like overlap integrals of the polarization cloud which is assumed to move coherently with the core hole. In molecules it will result in reduced splittings of the various symmetry molecular orbitals.

The other extreme approach is to do a symmetry-restricted calculation in which the core-hole wave function is a Bloch wave function in a solid or molecular orbital in a molecule. In this kind of calculation one is forced to do a considerable amount of CI to get any screening at all. In metals, for example, one would have to take an infinite number of excited configurations into account to describe a deep core electron binding energy. The questions then arise: What should one do, and when? In the calculation of the binding energy of a 1s electron in O_2 , for example, Bagus¹ has shown that considerably better results can be obtained using a symmetry unrestricted calculation in which the core hole is found to be localized. On the other hand, it is usually assumed that valence electron excitations or ionizations can be described with symmetry restricted calculations.

The quantities which are important in determining which approximation is the better are (1) the hole delocalization time τ_c which is determined by the transfer

integral of a hole between two sites or, in solids, the bandwidth of the hole $\tau_c = \hbar/\Delta E_c$; (2) the electric field or gradient of the Coulomb potential felt by the other electrons due to a local hole; and (3) the response time τ_v of the other electrons which is determined by the transfer integral or bandwidth of the valence electrons for unfilled bands or molecular orbitals and the excitation energies from filled bands or orbitals.

To investigate this problem in more detail, we do a model calculation in which the three relevant interactions can be varied and for which an exact solution is possible which then can be compared with the solutions of the localized and delocalized approximations. We consider the 1s photoelectron spectrum of the fictitious molecule Li_2^+ with electron configuration $\sigma_{1g}^2, \sigma_{1u}^2, \sigma_{2g}^1$, with σ_1 composed of 1s atomic orbitals and σ_2 of 2s atomic orbitals. To avoid complications due to spin multiplicities, we take the 2s electrons to be spin up and neglect exchange interactions with the 1s electrons. The ground state wave function is

$$\Psi_g = \frac{1}{\sqrt{5!}} |\Psi_{1s_A}^1 \Psi_{1s_A}^1 \Psi_{1s_B}^1 \Psi_{1s_B}^1 \Psi_{2g}^1|.$$

We consider a Hamiltonian with only the matrix elements

$$\langle \Psi_{1s_A}^1 | H | \Psi_{1s_B}^1 \rangle = T_{1s}, \quad \langle \Psi_{1s_A}^1 | H | \Psi_{1s_A}^1 \rangle = E_{1s},$$

$$\langle \Psi_{2s_A}^1 | H | \Psi_{2s_B}^1 \rangle = T_{2s}, \quad \langle \Psi_{2s_A}^1 | H | \Psi_{2s_A}^1 \rangle = E_{2s},$$

$$\langle \Psi_{1s_A}^1 \Psi_{2s_A}^1 | H | \Psi_{1s_A}^1 \Psi_{2s_A}^1 \rangle = Q,$$

$$\langle \Psi_{1s_A}^1 | \Psi_{1s_B}^1 \rangle = 0, \quad \langle \Psi_{2s_A}^1 | \Psi_{2s_B}^1 \rangle = 0.$$

These matrix elements are directly related to the three important quantities discussed above. We could also include the other Coulomb interactions which, however, add nothing new to the physics involved.

Within this model it is easy to determine the 1s photoelectron spectrum. The positions of the peaks are determined by the eigenvalues of the states with one 1s electron removed, and the intensities are given in the sudden approximation by

$$I \propto |\langle \Psi_f(1s) | \Psi_g(1s) \rangle|^2 \quad (1)$$

where $\Psi_f(1s)$ is the frozen-state wave function with a hole in the 1s orbital and $\Psi_g(1s)$ is the eigenfunction of

the final state with a hole in the 1s orbital. The energies of the possible final states are given by

$$E_i = 3E_{1s} + E_{2s} + Q + \omega_i,$$

with

$$\omega_i = \frac{Q \pm \sqrt{Q^2 + 4(T_{2s} \pm T_{1s})^2}}{2}, \quad (2)$$

resulting in four possible final states. Subtracting the energy of the ground state, we obtain binding energies of

$$\epsilon_b^{1s} = -E_{1s} + T_{2s} - \frac{Q \pm \sqrt{Q^2 + 4(T_{2s} \pm T_{1s})^2}}{2} \quad (3)$$

$$(E_{1s} < 0, T_{2s} > 0, Q > 0).$$

The lowest binding energy corresponding to the energy of an adiabatic ionization is given by

$$\epsilon^{1s} = -E_{1s} + T_{2s} - \frac{Q + \sqrt{Q^2 + 4(T_{2s} + T_{1s})^2}}{2}. \quad (4)$$

We want to compare these solutions to those of localized and delocalized approximations. The delocalized symmetry restricted solutions without configuration interaction are easily obtained yielding

$$\epsilon_b^{1s}(DL) = -E_{1s} - \frac{Q}{2} \pm T_{1s}, \quad (5)$$

corresponding to the bonding and antibonding combinations of 1s orbitals. In the photoelectron spectrum these lines will have equal intensity. The localized solutions can be obtained by simply setting $T_{1s} = 0$ in Eq. (3) yielding

$$\epsilon_b^{1s}(L) = -E_{1s} + T_{2s} - \frac{Q \pm \sqrt{Q^2 + 4T_{2s}^2}}{2}. \quad (6)$$

Unlike the localized solution, the delocalized solution cannot be simply obtained from the exact solution. The two lines obtained from the localized solution are easily identified with the problem of a diatomic molecule discussed by Hush.² The intensities of these lines are obtained using Eq. (1) with final state wave functions:

$$\begin{aligned} \Psi_F^*(1s^A) &= C_1^* \Psi_{1sA}^* \Psi_{2sA}^* + C_2^* \Psi_{1sA}^* \Psi_{2sB}^*, \\ \Psi_F^*(1s^B) &= C_1^* \Psi_{1sB}^* \Psi_{2sB}^* + C_2^* \Psi_{1sB}^* \Psi_{2sA}^* \end{aligned} \quad (7)$$

(1s^A in brackets refers to the 1s hole on atom A), where $\Psi_{1sA,B}^*$ refers to a hole in the 1s orbital of atom A or B and $\Psi_{2sA,B}^*$ refers to an electron in the 2s orbital of atom A or B. These wave functions reveal the correlation between the core hole and the 2s electron and, more explicitly, give the probability amplitude of the 2s electron being on the same or other site as the core hole. The coefficient $(C_1^*)^2$ gives the probability that the 2s electron is on the same site as the core hole for the lowest binding energy state. This is shown in Fig. 1 as a function of Q/T_{2s} . For $Q \gg T_{2s}$ the 2s electron moves in to completely screen the core hole. The coefficients $C_{1,2}^*$ are given by

$$C_1^* = \sqrt{\frac{2T_{2s}^2}{Q^2 + 4T_{2s}^2 \pm Q\sqrt{Q^2 + 4T_{2s}^2}}}, \quad (8)$$

$$C_2^* = \frac{(Q \pm \sqrt{Q^2 + 4T_{2s}^2})}{2T_{2s}} C_1^*. \quad (9)$$

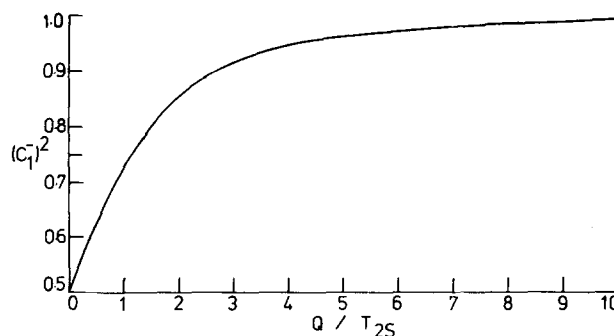


FIG. 1. The probability that the 2s electron is on the same site as the core hole as a function of Q/T_{2s} , assuming the core hole to be localized on a particular site.

We see that, in the localized description, the two states corresponding to +, - in Eq. (6) are each doubly degenerate because of the two possible positions of the localized hole. The intensities of the two lines are given by

$$I^\pm = \frac{1}{2}(1 + 2C_1^* C_2^*) \quad (10)$$

To see what these two solutions mean, we look at some limiting cases. For $Q \ll T_{2s}$ we find two lines at approximately $\epsilon_b = -E_{1s}$ and $\epsilon_b = -E_{1s} + 2T_{2s}$ with intensities of approximately $1 - (Q^2/T_{2s}^2)$ and Q^2/T_{2s}^2 , respectively. These correspond to a main line and a shakeup satellite in which the 2s electron has been excited to the antibonding orbital.

In the other limit, i.e., $T_{2s} \ll Q$, we again get two lines at

$$\epsilon_b = -E_{1s}$$

and

$$\epsilon_b = -E_{1s} - Q$$

corresponding to the ionization of Li^+ and Li^0 with approximately equal intensities. As pointed out by Hush,² the spectrum now looks like that of a mixed valence compound, which it obviously is not in the ground state. A direct comparison can be made with the results obtained by Hush² by setting $\alpha = 2T_{2s}/Q$ and realizing that $C_1^* C_2^* = -C_1^* C_2^*$ so that the intensity ratio of the two peaks is given by

$$\frac{I^+}{I^-} = \frac{[1 + (1 + \alpha^2)^{1/2} - \alpha]^2}{[1 + (1 + \alpha^2)^{1/2} + \alpha]^2},$$

as found by Hush.²

We now return to the original problem of comparing the localized and delocalized calculations to the exact one. There is, as mentioned in the introduction, one other rather obvious thing we should do with the localized calculation. As mentioned above, the two states found are each doubly degenerate because of the two possible positions of the core hole. This degeneracy will be lifted as soon as we turn on the transfer integral T_{1s} , and will result in eigenstates which have the symmetry of the molecule. Taking into account only an interaction between the degenerate states, we get new eigenfunctions [from Eq. (7)]

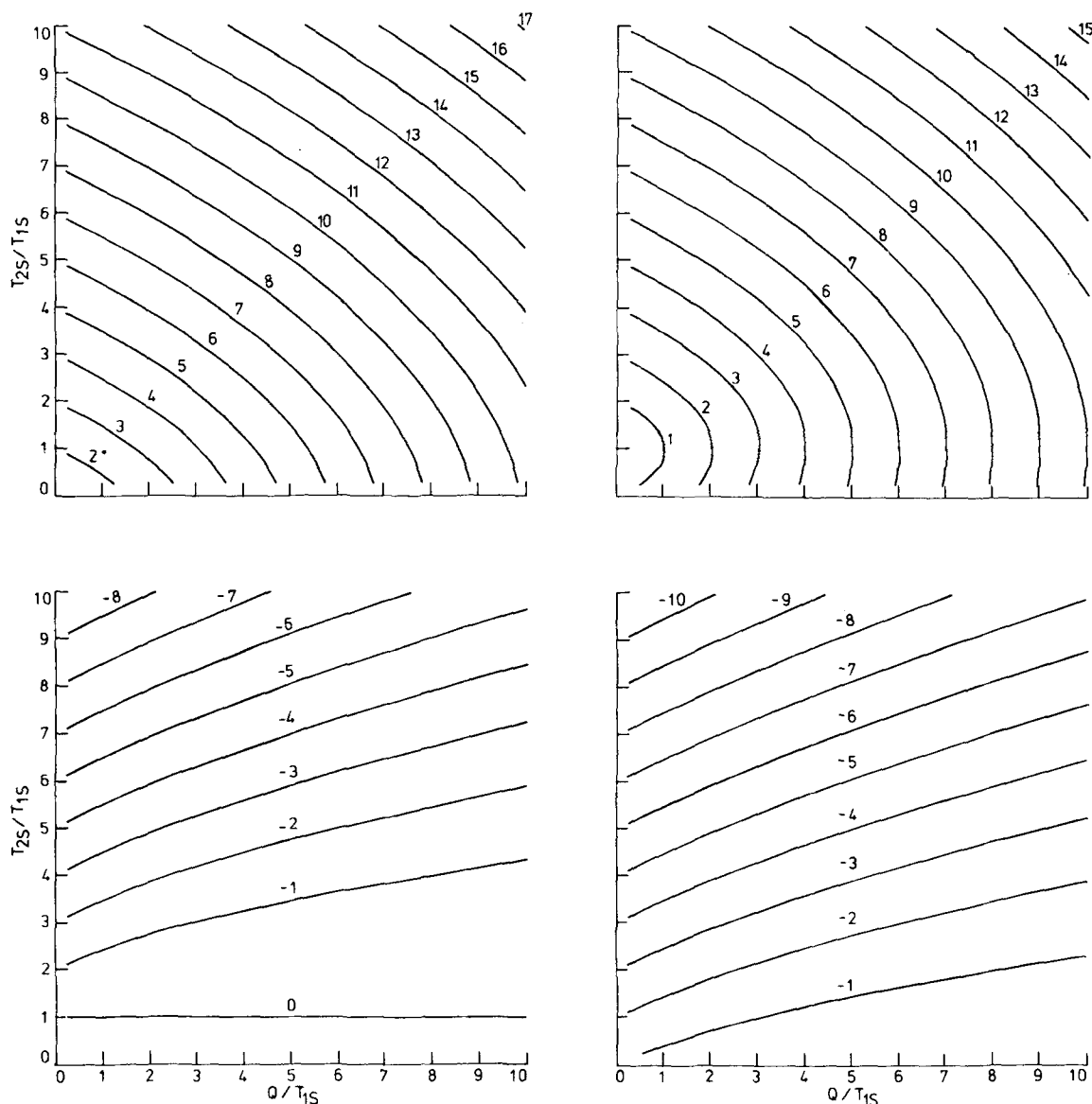


FIG. 2. The constant energy curves in units of T_{1s} for the four levels obtained from the exact solution, as a function of T_{2s}/T_{1s} and Q/T_{1s} . The zero of energy is taken to be equal to E_{1s} .

$$\Psi_{Fb}^{\pm} = \frac{1}{\sqrt{2}} [\Psi_F^{\pm}(1s^A) + \Psi_F^{\pm}(1s^B)] \quad ,$$

$$\Psi_{Fa}^{\pm} = \frac{1}{\sqrt{2}} (\Psi_F^{\pm}(1s^A) - \Psi_F^{\pm}(1s^B)) \quad , \quad (11)$$

corresponding to the bonding and antibonding states of the hole plus its polarization cloud, respectively. Since the only term neglected in the Hamiltonian to obtain the localized solutions was that involving the one-electron transfer integral T_{1s} , this will be the only term causing the splitting between the bonding and antibonding states. Of course, this term will also mix $\Psi_F^{\pm}(1s^A)$ with $\Psi_F^{\pm}(1s^B)$ which for this simple molecule could also be taken into account, in which case we would get the exact result. This mixing will however not be as important because these states are well separated in energy. Also, we are trying here to set up a procedure which can also be applied to much larger molecules and solids, in which case the mixing of only the degenerate states remains

a well-defined and relatively simple procedure. The splitting of the bonding and antibonding states will be given by

$$2\langle \Psi_F^{\pm}(1s^A) | H | \Psi_F^{\pm}(1s^B) \rangle \quad ,$$

which will be considerably less than $2T_{1s}$, because $\Psi_F^{\pm}(1s^A)$ and $\Psi_F^{\pm}(1s^B)$ are not one-electron or one-hole wave functions but include the polarization cloud. In terms of the wave functions given by Eqs. (11) and (7), the splitting of the bonding and antibonding states is given by

$$\Delta\epsilon^{\pm} = 4C_1^{\pm}C_2^{\pm}T_{1s} \quad , \quad (12)$$

which is strongly reduced from $2T_{1s}$, because $C_1^{\pm}C_2^{\pm} < \frac{1}{2}$. The coefficient $C_1^{\pm}C_2^{\pm}$ is just the overlap integral of the polarization cloud for the hole on atom A with that for the hole on atom B.

For example, the lowest binding energy peak would now come at

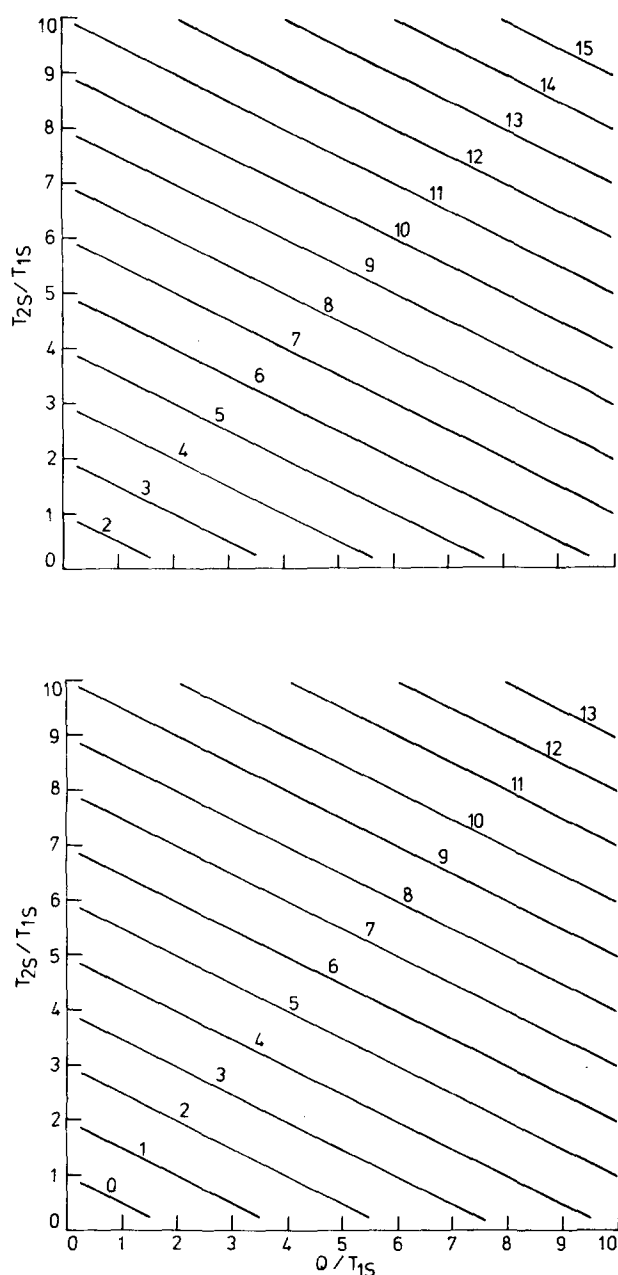


FIG. 3. The constant energy curves in units of T_{1s} for the two levels obtained from the symmetry restricted solution as a function of T_{2s}/T_{1s} and Q/T_{1s} .

$$\epsilon_b^1(L, \text{Sym}) = -E_{1s} + T_{2s} - \frac{Q + \sqrt{Q^2 + 4T_{2s}^2}}{2} - 2 \frac{(Q + \sqrt{Q^2 + 4T_{2s}^2})T_{2s}T_{1s}}{Q^2 + 4T_{2s}^2 + Q\sqrt{Q^2 + 4T_{2s}^2}} \quad (13)$$

(Sym stands for symmetrized). It should be noted that this procedure is easily carried out for larger molecules or for solids, in the latter case corresponding to the electronic polaron.

We now want to compare these solutions to the exact ones for various values of T_{2s} , T_{1s} , and Q . Since these are free parameters, we can also look at what happens for $T_{1s} \approx T_{2s}$ or $T_{1s} > T_{2s}$, corresponding to the photoelectron spectrum of a valence orbital. We first of all note that

for the lowest binding energy peak for $Q \rightarrow 0$ both $\Psi_b^1(\text{DL})$ and $\Psi_b^1(L, \text{Sym})$ give the same result and are equal to the exact result for all values of T_{2s} and T_{1s} . This is rather interesting since here we would have expected the localized description to break down, but the symmetrization after doing the localized hole calculation again results in the exact solution for this limit. Also, in the other limit where $Q \gg T_{2s}$ and $Q \gg T_{1s}$ the localized solution results in the exact value whereas the delocalized solution is in error by $Q/2$ for the lowest binding energy peak. Also, in the limit that Q and $T_{2s} \gg T_{1s}$ the localized description is exact whereas the delocalized description is far from the exact result. This already indicates that perhaps the localized description with symmetrization is almost always the better procedure.

To show this in more detail we have plotted in Figs. 2(a) to (d) the constant energy curves for the four peaks of the exact solution in units of T_{1s} and as a function of T_{2s}/T_{1s} and Q/T_{1s} . In Figs. 3(a) and (b) the same plots are shown for the delocalized solutions, and in Figs. 4(a) to (d) for the localized solution with (solid) and without (dashed) symmetrization. From these plots we see that for large Q or large T_{2s} the delocalized solution clearly breaks down. Surprisingly, the localized solution with symmetrization afterwards agrees very well with the exact solution over a large range of Q and T_{2s} . This is especially so for the lowest and highest binding energy peaks. The central two peaks are expected to deviate more from the exact result because these have a smaller energy separation so that the neglect of $\Psi_F^-(1s^A)$ with $\Psi_F^+(1s^B)$ mixing in Eqs. (11) and (13), respectively, will be more important.

Of primary interest is the position of the lowest binding energy peak corresponding to an adiabatic ionization. In Figs. 5(a) and (b) we show constant energy difference curves between the exact and the localized solution with symmetrization, and the delocalized solution (again in units of T_{1s} and as a function of T_{2s}/T_{1s} and Q/T_{1s}). Also shown in Fig. 5(a) is the curve on which the localized and delocalized solutions are equal. For all values of T_{2s}/T_{1s} and Q/T_{1s} larger than the boundary given by the curve $T_{2s}^2 + 4Q^2 = T_{1s}^2$ the localized solution is better except for $Q=0$, in which case the two are equal. This is rather interesting because we find that for all values of $T_{2s}/T_{1s} > 1$ independent of Q the localized solution with symmetrization afterwards is the better one. This means that even for the outer *valence electrons* the localized calculation with symmetrization will yield better results in many cases. We also find that for $Q/T_{1s} > 2$ independent of T_{2s} the localized solution gives better results. This limit is certainly satisfied by most core electrons and also for excitations out of lone pair orbitals.

Although this is a simple model calculation it does take into account the three kinds of important interactions for this problem, and we might therefore generalize the conclusions to larger molecules and solids. To do this it is more convenient to talk in terms of characteristic times rather than interactions. The three times involved in general are (1) the delocalization time τ_c of the hole created by the excitation which in our case is $\tau_c = \hbar/T_{1s}$; (2) the characteristic interaction time τ_i with the polar-

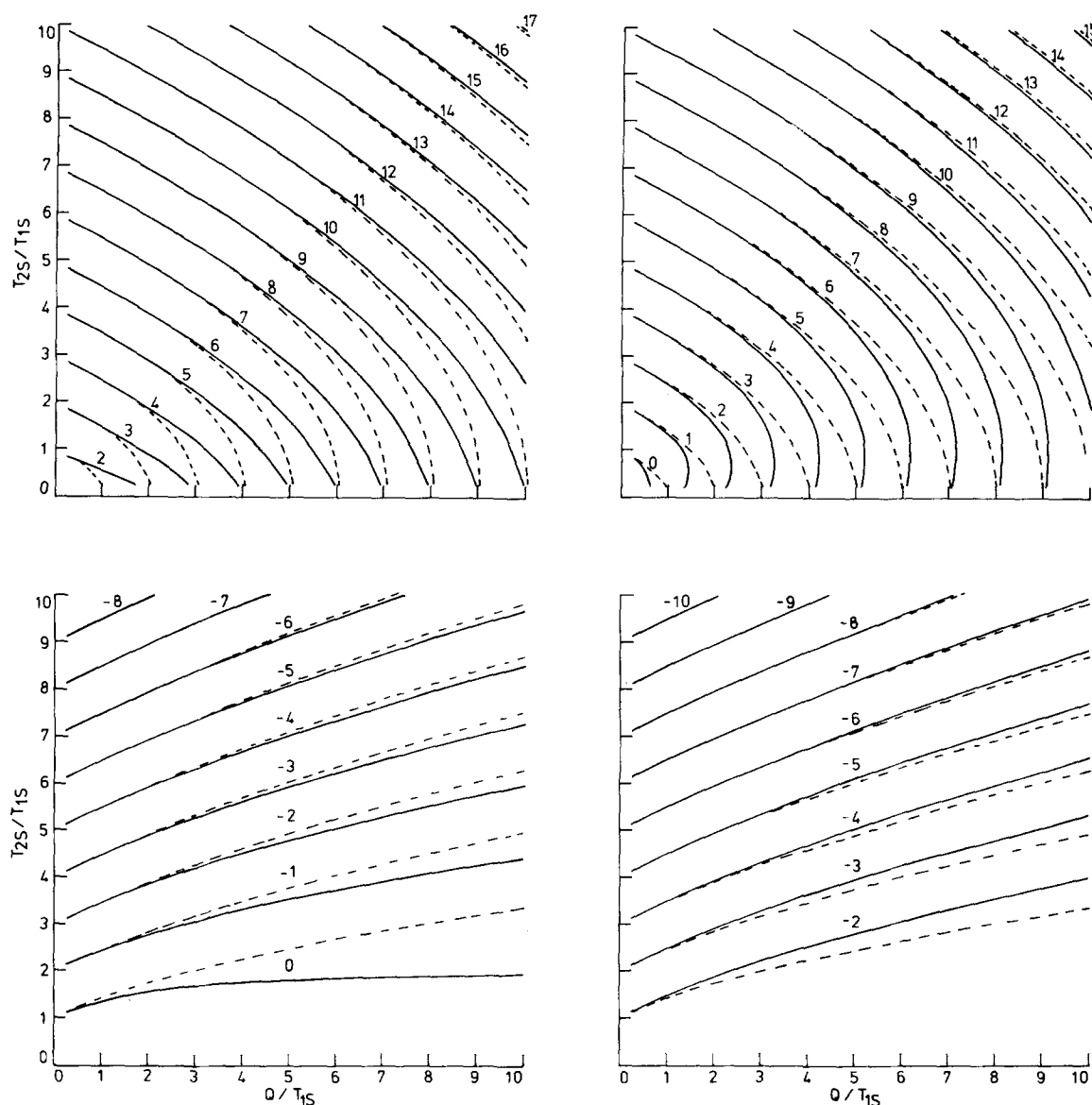


FIG. 4. The constant energy curves in units of T_{1S} for the levels obtained from the localized solution before (dashed) and after (solid) symmetrization.

izable medium which in our model is $\tau_I = \hbar/Q$ (as noted in the introduction, Q represents the electric field produced by a localized hole or the gradient of the potential felt by the polarizable medium); and (3) the response time τ_v of the polarizable medium which in our model is $\tau_v = \hbar/T_{2s}$. The conclusion then is that for $\tau_v < \tau_c$ or for $\tau_I < \frac{1}{2}\tau_c$ the localized description with symmetrization is preferable. Of course, in a general system the polarizable medium consists of many different parts each with its own characteristic response times. For example, core orbital polarization is a fast process in which the response time is given by $\hbar/\Delta E$, where ΔE is an excitation energy of the core electron involved. The valence electron response times will be determined by molecular orbital splittings in molecules and by bandwidths (metals) and band gaps (semiconductors) in solids.

From the calculation on the Li_2^+ model we conclude that the localized calculation is preferable in most cases, and also for the valence orbitals. This calculation

with symmetrization afterwards is equivalent to an electronic polaron model. The assumption inherent in this calculation is that the polarization cloud, formed by the other electrons (both core and valence), can respond quickly enough to coherently follow the motion of the hole as it jumps from atom to atom in the molecule or solid. In a delocalized or symmetry restricted calculation one assumes that the polarization cloud cannot follow the motion of hole. In this case the response of the system calculated for a delocalized hole results in a smaller relaxation energy as compared to a localized calculation.

The procedure the authors envision for the electronic or rather hole polaron calculation in a more realistic molecule or solid is as follows: We start with a symmetry restricted Hartree-Fock calculation of the ground state of the system described by a single Slater determinant of one-electron molecular orbitals. We assume that each of the so obtained molecular orbitals can be

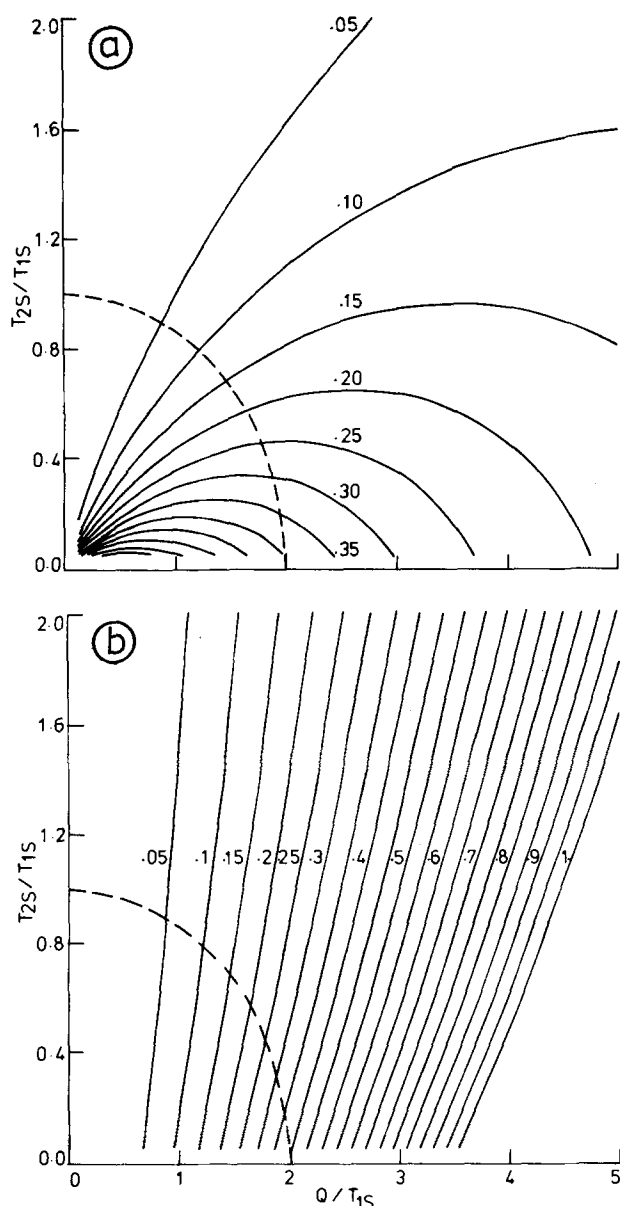


FIG. 5. The constant energy difference curves in units of T_{1s} for the lowest binding energy level between the exact and the symmetry restricted solution (b) and the exact and the localized solution (a). Also shown is the boundary curve on which the two solutions are equal. The localized solution with symmetrization afterwards is better for all values of T_{2s}/T_{1s} and Q/T_{1s} outside of the region enclosed by the boundary curve.

expressed in terms of a linear combination of atomic orbitals. We then do another Hartree-Fock calculation on an $N-1$ electron system with the constraint that one of the atomic orbitals, say on atom i , which is a component of the molecular orbital of interest is kept unoccupied. This can be done for example by removing all the terms in the Hamiltonian connecting this orbital with others. The ground state wave functions so obtained involves a single Slater determinant of $N-1$ electrons and the hole. This forms the polaron or a quasiparticle consisting of a local hole and its polarization cloud. We do this for all the atomic orbitals which appear as components of the molecular orbital of interest, realizing of course that all atoms related by symmetry operations

will give equivalent wave functions. We now have a set of n Slater determinants each involving $N-1$ electrons and a hole. We use this as a basis for the symmetrization. We now switch on the part of the Hamiltonian which we had removed before, obtaining again a set of molecular orbitals. The molecular orbitals however are no longer a combination of one-electron atomic orbitals but a combination of $N-1$ electron Slater determinants. Because of this all the off-diagonal matrix elements of the Hamiltonian will be reduced by the $N-1$ electron overlap integrals.

This procedure is by no means exact and may give rise to difficulties in open shell systems. The reason for suggesting it is mainly because it is a fairly well defined procedure which is identical to the procedure used in the Li_2^+ calculation for which we have shown the validity for a large range of parameters. Also we should note that this procedure includes the atomic relaxation contribution with an expected high degree of accuracy.

It would be of interest to test this procedure on diatomic and polyatomic molecules and compare it to Δ SCF and symmetry unrestricted calculations.

It should be noted that the above is not unrelated to the exciton model introduced by Ley *et al.*³ to describe relaxation energies. Here it is assumed that a whole valence electron is pulled into the site with a core hole. As can be seen from Fig. 1, this is expected to be a reasonable approximation if the Coulomb interaction is comparable to or larger than the molecular orbital splitting in molecules or bandwidths in solids.

It should be noted that the same kind of arguments holds for the optical spectra of molecules except that here the interaction of the hole with the excited electron must also be taken into account. Especially interesting are excitation spectra involving lone pair orbitals as in parabenzoquinone^{4,5} and PNDA⁶ which indeed are better described in a localized way with symmetrization afterwards which in this case leads to an excitonlike description.⁷

ACKNOWLEDGMENTS

The authors would like to thank C. Haas, W. Nieuwpoort, and J. Kommandeur for helpful discussions. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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